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14. ABSTRACT

Microfluidic devices for analyzing ionic pollutants in water were developed and characterized. Different device materials were tested with cyclic olefin copolymer (COC) being determined as the most suitable for long term depolyment. Subsequent testing involved challenging the devices with samples containing high ionic strength samples. A method was developed for removing the majority of the interfering high concentration species using solid phase extraction. Using the method, detection limits were approached for appropriate detection of perchlorate in ground water.

15. SUBJECT TERMS

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Final Report for W9132T-10-2-0012

Objectives:
1) Develop modular glass microchips for perchlorate analysis.

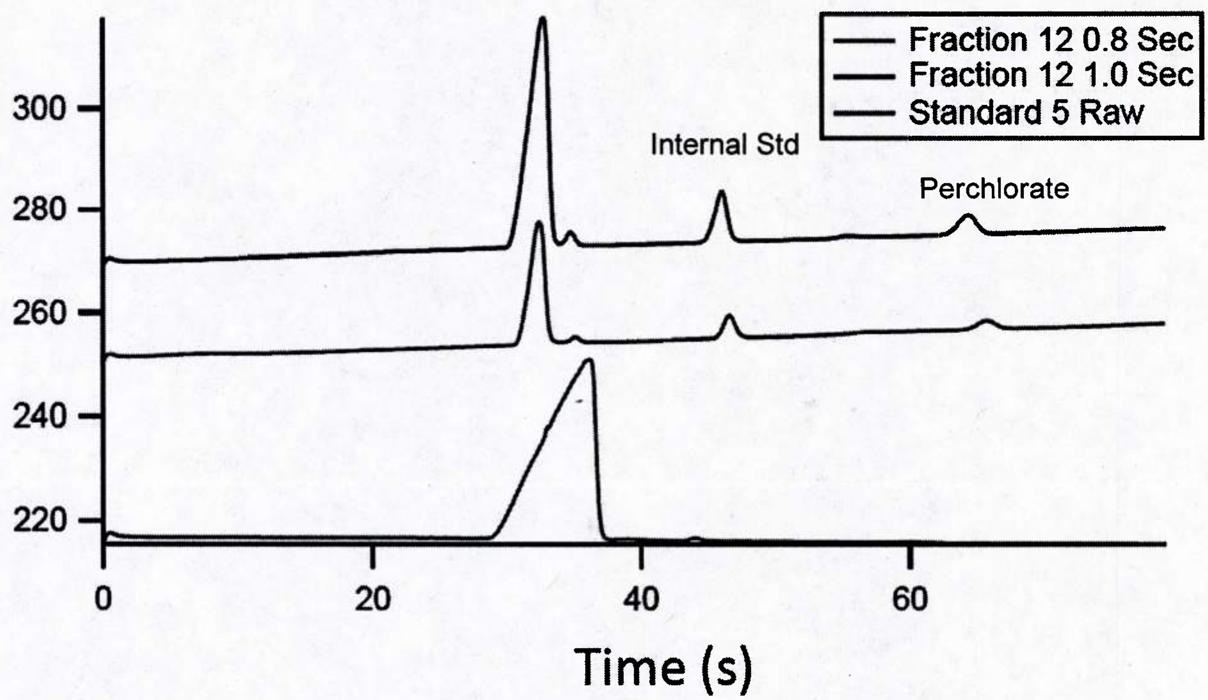
We attempted to make modular chips for this application but were unsuccessful due to the problems with the high bonding tempature of glass and the melting point of the metals we used. As a result, we focused more on studies done comparing PDMS, PMMA, PC, and COC microchips for contact conductivity detection for ion separations.

2) Compare modular glass microchips to PDMS and PMMA microchips.

Once learning we were not able to make glass microchips, we focused on comparing the performance of PDMS, PMMA, PC, and COC (cyclic olefin copolymer). These polymers were chosen because they are the most common polymers used in microfluidics and can be manufactured via a wide range of methods including molding and hot embossing. In our initial comparison steps, we compared separation efficiency, migration time reproducibility, and peak area reproducibility. PDMS and COC proved to be the most consistent with PMMA and PC showing substantial variability from batch to batch of the material. As a result, further evaluations were made between PDMS and COC. In comparing COC to PDMS, two major trends were noted. First, the migration times of perchlorate under identical buffer conditions were always longer, by 20% for COC microchips versus PDMS. PDMS microchips also gave more defined (sharper) peaks than the COC. Both chip materials, however, were able to resolve perchlorate from competing ions with ease and thus it is proposed that COC microchips be used going forward because they are easier to manufacturing using injection molding on an industrial scale. They are also easier to work with because they are rigid polymers.

3) Challenge perchlorate separation with multiple concentrations of anions and include the ability to generate a calibration curve.

One major limitation of microchip electrophoresis is the potential for high ionic strength samples containing excess sulfate and/or chloride to prevent the system from functioning properly. As a result, we tested multiple approaches to quantifying part-per-billion levels of perchlorate in the presence of millimolar concentrations of sulfate and chloride. In the absence of any purification methods, perchlorate detection limits were 100 ppb with 1 mM each chloride and sulfate. To address this problem, we have explored use of OnGuard cartridges produced by ThermoFisher Scientific. The cartridges contain a resin with Ba and Ag. Ba reacts strongly with sulfate forming insoluble $BaSO_4$, while Ag reacts with chloride to produced insoluble AgCl. The figure below shows electropherograms for before the sample was passed through the column (blue, bottom trace) and then after the material has been purified (red and black trace). The sample consisted of 1 mM each of chloride and sulfate and 25 ppb perchlorate. Two injection times were used to verify that the peaks were real and not system peaks. These results clearly show our ability to analyze perchlorate in these complex samples using the OnGuard columns.



Fraction 12 0.8 Sec
Fraction 12 1.0 Sec
Standard 5 Raw
Internal Std
Perchlorate
300
280
260
240
220
0
20
40
60
Time (s)